

Development and Performance of the W/Sb₂O₃/KIO₄/Lubricant Pyrotechnic Delay in the US Army Hand-Held Signal

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Abstract: Gassy pyrotechnic delays composed of tungsten, antimony(III) oxide, potassium periodate, and various lubricants have been developed for use in the US Army hand-held signal. The new compositions were developed to replace the current formulation, which contains potassium perchlorate and barium chromate, chemicals that are facing increasing scrutiny due to environmental regulation. The hand-held signal delay housing was used to demonstrate the burning rate tunability of the new compositions.

Keywords: Pyrotechnic delays • Tungsten • Periodate • Hand-held signal

The addition of 1–5% of waxy lubricants (stearic acid or calcium stearate) was found to have a profound effect on burning rate. The effect of tungsten content and the Sb₂O₃/KIO₄ ratio on burning rate was also probed. A wide range of inverse burning rates (2 to 15 s cm^{−1}) were demonstrated, which encompasses the 7 to 8.5 s cm^{−1} range required by the hand-held signal. The W/KIO₄ reaction produces I₂, which was observed by visible spectroscopy in the vapor above a sample of combustion residue.

1 Introduction

Pyrotechnic delays have long been used in munitions to provide reproducible time intervals between energetic events. US Army hand-held signals (HHS) are used for battlefield signalling and illumination [1]. They contain a rocket motor and pyrotechnic payload inside an aluminum launch tube. When the primer at the base of the tube is struck, an initiating charge burns and ignites the rocket propellant. Hot propellant gases ignite a delay element that burns as the rocket reaches its apex. This delay element then ignites an expulsion charge, which ejects and ignites the smoke or illumination payload.

The current delay composition used in HHS consists of 32.0% tungsten, 56.3% barium chromate, 11.4% potassium perchlorate, and 0.3% VAAR. (All composition percentages in this article are weight percentages.) This composition is a variant of the traditional tungsten delay, MIL-T-23132A, which contains diatomaceous earth as a diluent and no polymeric binder. Compositions of this type are highly tunable [2]. Varying the W/BaCrO₄ ratio and the metal particle size gives inverse burning rates ranging from 0.06 to 15 s cm^{−1} [3,4]. However, chromates and perchlorates face increasing environmental scrutiny and regulation [5,6]. The US Army is therefore searching for viable alternatives to these chemical compounds.

Under the US Army's Environmental Quality Technology Program, a project was initiated to develop a chromate-free and perchlorate-free delay composition for hand-held signals. The HHS delay housing is a 14.5 gram pancake-shaped piece of aluminum (2024-T4) that doubles as

a structural component of the rocket (Figure 1). A black powder input charge, the delay composition, and a black powder output charge are loaded into the off-center



Figure 1. The hand-held signal delay housing. The output side (4.8 mm diameter hole) is shown in this photograph.

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4.8 mm diameter cavity, which is only 10.2 mm long. In the rocket, the input charge is lit from a small (1.9 mm diameter) hole on the opposite side of this cavity. Since the black powder input and output charges collectively occupy 3 mm of length, there is only about 7 mm left for the delay composition, which must burn for 5 to 6 seconds. Therefore, an inverse burning rate of 7 to 8.5 scm^{-1} is required.

The large thermal mass of the HHS delay housing, combined with the long burning time requirement and short burning path, make it particularly difficult to find suitable replacement compositions. In addition, for this application the replacement composition must be lit reliably by black powder, which has a relatively low flame temperature [7]. We have recently reported that the ternary $\text{Si/Sb}_2\text{O}_3/\text{Bi}_2\text{O}_3$ system may be ignited by black powder and is able to function in thick aluminum tubes [8], but burning rates suitable for the HHS could not be achieved in these tubes or the HHS delay housing due to thermal quenching of the slower-burning compositions.

Despite all the difficulties imposed by the HHS delay housing configuration, one advantage of the system is that the delay composition need not be gasless. This is due to the design of the rocket, in which 15% of the delay cavity volume is occupied by the black powder input charge that vents gases to the propellant combustion chamber; the delay composition also vents to this chamber. Rugunanan and Brown studied the gassy Si/KNO_3 system and achieved burning rates as slow as 1.7 mm s^{-1} (5.9 scm^{-1}) at low silicon percentages in stainless steel channels [9]. We obtained an inverse burning rate of 3.5 scm^{-1} with a 35% Si composition pressed in aluminum tubes, but it was thermally quenched by the HHS delay housing.

Faced with these challenges, we returned to the traditional $\text{W/BaCrO}_4/\text{KClO}_4$ composition for inspiration. In this

system, BaCrO_4 serves as the primary “slow” oxidizer, while KClO_4 (the “fast” oxidizer) serves to sustain the reaction and sensitize the composition for ignition [2]. In this work, we chose to examine Sb_2O_3 as a BaCrO_4 replacement. In Si-based systems, it is known that Sb_2O_3 and the related Sb_6O_{13} give relatively slow burning rates in comparison to Bi_2O_3 [8–11]. While Sb_2O_3 is not completely benign from a health and environmental standpoint [12], it is arguably an improvement over chromates, which are confirmed carcinogens [6]. As a KClO_4 replacement, we have examined potassium periodate (KIO_4). This oxidizer has been known to researchers in pyrotechnics since the 1960s, if not earlier [13]. Periodate salts have recently been proposed as replacements for KClO_4 in flash/incendiary compositions such as IM-28 [14]. Unlike ClO_4^- , the IO_4^- ion is not expected to compete with I^- in the thyroid gland [15].

2 Experimental Section

2.1 Material Properties

Tungsten (MIL-T-48140, type 2) was obtained from Atlantic Equipment Engineers. Potassium periodate (A11308), antimony(III) oxide (senarmontite A11123) [16], calcium stearate monohydrate (39423), and hexagonal boron nitride (11078) were obtained from Alfa Aesar. Graphite (282863) and polytetrafluoroethylene (430943) were obtained from Sigma Aldrich. Stearic acid (19–5010) was obtained from Hummel Croton. A Malvern Morphologi G3S optical microscopy particle size analyzer was used to determine number-based CE diameter distributions; volume-based distributions were calculated (Table 1).

Scanning electron microscopy (SEM) was performed with an Evex Mini-SEM SX3000 operating at 25 keV and

Table 1. Particle size data/ μm .

Material (Formula)	CE Diam. ^{a)} (D[4,3]) ^{b)}	D[n, 0.1] ^{c)} (D[v, 0.1]) ^{d)}	D[n, 0.5] ^{c)} (D[v, 0.5]) ^{d)}	D[n, 0.9] ^{c)} (D[v, 0.9]) ^{d)}
Tungsten (W)	4.51 (26.57)	1.73 (6.46)	3.46 (18.58)	8.23 (61.25)
Potassium periodate (KIO_4)	4.23 (66.75)	1.29 (26.08)	2.66 (64.36)	7.38 (103.8)
Antimony(III) oxide (senarmontite, Sb_2O_3)	5.39 (57.86)	1.68 (9.15)	4.17 (35.47)	10.05 (126.9)
Calcium stearate ($\text{C}_{36}\text{H}_{70}\text{O}_4\text{Ca}\cdot\text{H}_2\text{O}$)	5.83 (22.23)	1.82 (7.84)	4.57 (19.54)	10.81 (36.60)
Graphite (C)	5.53 (15.81)	2.03 (6.22)	4.57 (11.96)	10.19 (22.99)
PTFE (C_2F_4) _x	9.92 (30.07)	2.91 (11.87)	8.21 (27.86)	18.61 (49.72)
Boron nitride (hexagonal, BN)	6.39 (21.79)	2.18 (7.16)	5.53 (14.16)	11.42 (42.68)
Stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$)	11.50 (90.01)	2.40 (29.36)	5.91 (83.92)	25.51 (154.5)

a) Number-based CE (circle-equivalent) mean diameter. b) Volume mean diameter. c) D[n, x] is the diameter at which (100·x)% of the number distribution is below. d) D[v, x] is the diameter at which (100·x)% of the volume distribution is below.

equipped with a secondary electron imaging (SEI) detector. The sample was affixed to the aluminum stub sample holder with a carbon adhesive tab. SEM indicated that the tungsten used in this study was agglomerates of 2–8 μm particles and much finer sub- μm particles.

2.2 Preparation of Delay Elements

The compositions are dry mixtures of three or four components. They were prepared by a combination of mixing (vibrational) and screening (80 mesh) steps. A die was machined to hold the HHS delay housing during the loading and pressing steps. Black powder (class 7, 40–100 mesh) was used for the input and output charges. Pressing was performed at 26.8 kpsi (184.6 MPa) with a 10 s dwell time on a Carver hydraulic press. To prepare each delay element, 50 mg black powder was added and tamped, followed by the first half of the delay composition, followed by pressing. Afterwards, the second half of the delay composition was added and tamped, followed by 50 mg black powder, followed by pressing. The input and output charges (the black powder) collectively occupied 3 mm of length in the cavity. The amount of delay composition was chosen so that the total column length, including the input and output charges, was 9.4 to 10.2 mm long.

2.3 Test and Analysis Protocols

Each finished delay element was held by a clamp with the small hole facing up. A small amount (20–30 mg) of loose black powder was placed on top of the small hole. This was ignited with an electrically heated nichrome wire. Digital video recordings were used to ascertain the time between ignition of the input and “first light” of the output. Inverse burning rates (s cm^{-1}) were calculated by subtracting the burning time of the black powder layers (collectively 0.3 s) and dividing the resulting times by the lengths of the consolidated delay compositions. Five delay elements were prepared and tested for each composition and the results were averaged; the standard deviations of these measurements were generally small.

Ejected combustion residue (smoke) was collected by burning delay composition pressed into small aluminum (2024-T3) tubes. These tubes had an inner diameter, outer

diameter, and length of 4.8 mm, 9.5 mm, and 15.2 mm, respectively. For these experiments no black powder was used and the columns were ignited with an electrically heated nichrome wire directly. The residue was captured in a stainless steel cup. Visible spectroscopy was performed with a Varian Cary 5000 UV/Vis/NIR spectrometer. The residue was placed in a Beckman gas cell with a 5 cm path length. Spectra (400–700 nm) of the vapor above the residue were recorded at room temperature and at two higher temperatures by warming the cell with a heat gun.

3 Results and Discussion

3.1 The W/Sb₂O₃/KIO₄ System and the Effect of Lubricants

A 40% W, 30% Sb₂O₃, 30% KIO₄ composition gave an inverse burning rate of 3.34 s cm^{-1} . However, pressing this composition was complicated by its abrasiveness that caused the tooling to bind on more than one occasion. The addition of 2% graphite alleviated this problem and also slowed the burning rate (4.60 s cm^{-1}). Other lubricants at the 2% level also increased burning times, some dramatically (Table 2).

All the lubricants improved composition packing comparably, with densities as a percentage of theoretical maximum (%-TMD) ranging from 88% to 92%. Graphite, PTFE, and hexagonal BN all caused a similar increase in inverse burning rate, whereas stearic acid and calcium stearate had a more pronounced effect. The calcium stearate composition burned at 7.26 s cm^{-1} , more than twice as long as the composition without added lubricant. These long burning times are attributed to the ability of stearic acid and calcium stearate to form a molten insulating wax layer ahead of the burning front. Stearic acid melts at 69°C [17] while calcium stearate monohydrate (the type used in this study) is dehydrated at $100\text{--}110^\circ\text{C}$, begins to soften at 125°C , and is molten by 160°C [18,19]. A similar effect was observed in B₄C/KNO₃/KCl smoke compositions, where small percentages of added calcium stearate increased burning times four-fold [20]. PTFE also melts although at a higher temperature, 333°C [21], and is a potent pyrotechnic oxidizer. Hexagonal BN melts at ca. 2600°C [22] and graphite sublimates above 3600°C [17].

Table 2. Effect of lubricants^{a)}.

Lubricant	Consolidated density/ g cm^{-3}	%-TMD ^{b)}	Inverse burning rate/ s cm^{-1}
None ^{c)}	5.07 (0.04)	79.7 (0.7)	3.34 (0.04)
Graphite	5.39 (0.05)	88.0 (0.8)	4.60 (0.07)
PTFE	5.46 (0.03)	89.1 (0.5)	4.70 (0.10)
BN (hex)	5.35 (0.05)	87.6 (0.8)	5.01 (0.08)
Stearic acid	5.11 (0.04)	89.5 (0.7)	6.17 (0.16)
Calcium stearate	5.34 (0.05)	92.3 (0.9)	7.26 (0.17)

a) Compositions containing 40% W, 30% Sb₂O₃, 30% KIO₄, and 2% additional lubricant consolidated at 184.6 MPa (standard deviations in parentheses). b) Consolidated density as a percentage of theoretical maximum. c) No lubricant was used.

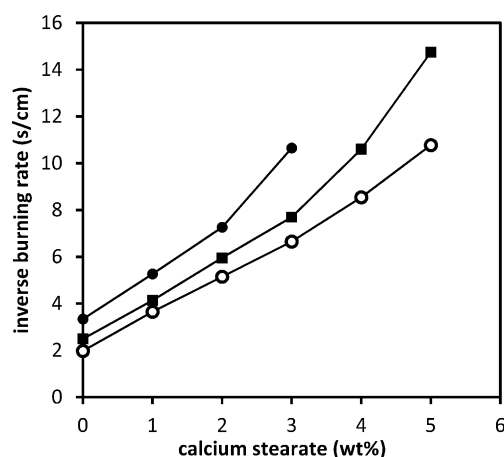


Figure 2. Effect of added calcium stearate on inverse burning rate – W/Sb₂O₃/KIO₄ ratios of 40/20/40 (bottom curve, open circles); 40/25/35 (middle curve, squares); 40/30/30 (top curve, closed circles). A consolidation pressure of 184.6 MPa was used.

Due to its large influence on burning rate, calcium stearate was selected for further studies. Compositions were prepared with three different Sb₂O₃/KIO₄ ratios (20/40, 25/35, and 30/30) while tungsten was held constant at 40% and the calcium stearate level was varied. As with the previous experiments, the lubricant was added in addition to the 100% balance of the primary components. A plot of inverse burning rate versus calcium stearate level shows three stacked curves, one for each oxidizer ratio (Figure 2). Generally, compositions with a lower Sb₂O₃/KIO₄ ratio burned more rapidly than comparable ones with a higher ratio, although these differences were small compared to the large influence of calcium stearate. Compositions with a 20/40 Sb₂O₃/KIO₄ ratio (bottom curve) spanned 1.98–10.78 s cm⁻¹, while those with a 25/35 ratio (middle curve) spanned 2.49–14.75 s cm⁻¹. The 30/30 Sb₂O₃/KIO₄ ratio (top curve) gave compositions that functioned with up to 3% added calcium stearate, spanning 3.34–10.65 s cm⁻¹; those with more lubricant only propagated partially and were thermally quenched. Extrapolation of this curve suggests that had these compositions not quenched, the resulting burn times would have been extremely long. Greater calcium stearate content also caused the compositions to consolidate more effectively (Figure 3).

In gassy pyrotechnic systems (such as the one in this study), an increase in loading pressure generally results in a decrease in burning rate [23]. This is due to a reduction in the number of void spaces, which allow combustion gases to migrate ahead of the burning front, preheating un-burnt layers [24]. To test the effect of loading pressure, a 45% W, 25% Sb₂O₃, 30% KIO₄, +2% calcium stearate composition was used to prepare delay elements in the standard HHS housings. As loading pressure was increased from 100 to 400 MPa, the %-TMD increased from 84% to 97% and the burning rate decreased by 25% from 0.20 to 0.15 cm s⁻¹. At a constant loading pressure, Figure 2 and

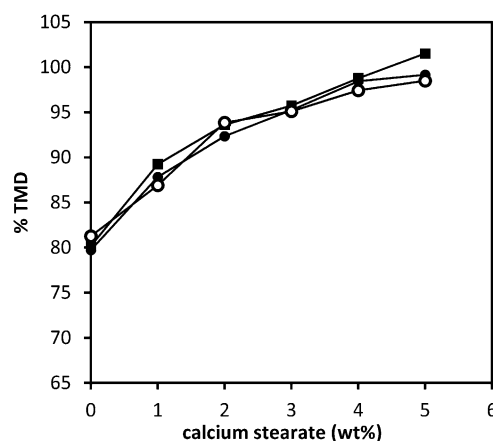


Figure 3. Effect of added calcium stearate on calculated %-TMD – W/Sb₂O₃/KIO₄ ratios of 40/20/40 (open circles); 40/25/35 (squares); 40/30/30 (closed circles). A consolidation pressure of 184.6 MPa was used.

Figure 3 show that increasing calcium stearate content results in improved consolidation and correspondingly slower burning rates, although the effect is greater than the changes in %-TMD alone would suggest. One reason for this may be the ability of molten calcium stearate to flow within the column, increasing the separation between fuel and oxidizer particles. Calcium stearate is also an insulator, and as its content increases the thermal conductivity of the column decreases. As described below, thermal conductivity plays a large role in determining burning rate.

3.2 The Effect of Metal Content and Oxidizer Ratio

In tungsten-based delay compositions, burning rate is known to be highly dependent on thermal conductivity, and therefore on tungsten content [2,24]. In the traditional W/BaCrO₄/KClO₄/diatomaceous earth (MIL-T-23132A) system, exothermicity peaks at 30% tungsten, while burning rate continues to rise as the tungsten content is increased to 60% and beyond [4]. A similar trend was observed in this study (Figure 4). When the Sb₂O₃/KIO₄ ratio was held constant at 1/1 and tungsten content was varied, compositions containing 2% added calcium stearate gave inverse burning rates from 8.39 s cm⁻¹ (35% W) to 3.95 s cm⁻¹ (60% W). Compositions containing 25% or 30% tungsten did not sustain propagation.

As shown in Figure 2, the Sb₂O₃/KIO₄ ratio affects burning rate. To study this effect further, compositions were prepared with 40% W and various amounts of Sb₂O₃ and KIO₄. All the compositions contained an additional 2% calcium stearate. As Sb₂O₃ was increased from 10–30% (at the expense of KIO₄) burning times nearly doubled (Figure 5). Compositions containing 35% or 40% Sb₂O₃ were thermally quenched.

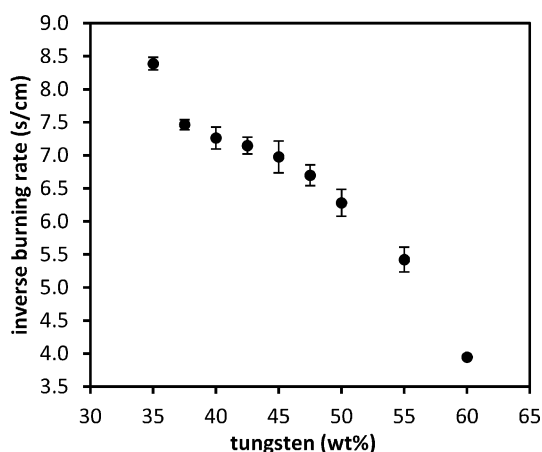


Figure 4. Effect of tungsten content on inverse burning rate. The Sb₂O₃/KIO₄ ratio was fixed at 1/1 as W varied from 25–60%. All contained an additional 2% calcium stearate. A consolidation pressure of 184.6 MPa was used. The error bars show two standard deviations.

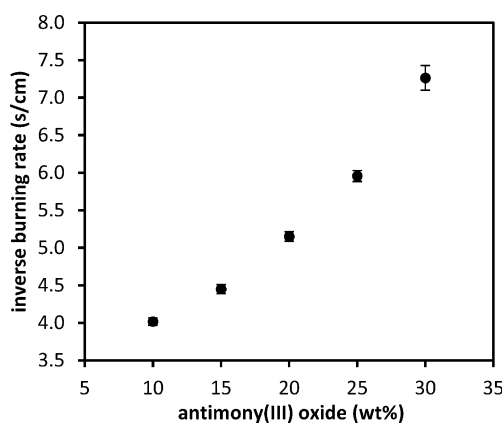


Figure 5. Effect of oxidizer ratio on inverse burning rate. Compositions contained 40% W, 10–40% Sb₂O₃, and KIO₄ (balance). All contained an additional 2% calcium stearate. A consolidation pressure of 184.6 MPa was used. The error bars show two standard deviations.

3.3 The Effect of Configuration

To test the effect of configuration in this study, a 40% W, 25% Sb₂O₃, 35% KIO₄, + 3% calcium stearate composition was used to prepare delay elements in the standard HHS housings, 2024-T3 aluminum tubes, and 304L stainless steel tubes. The tubes had the same inner diameter as the HHS housing cavity but were longer, 15.2 mm, and had an outer diameter of 9.5 mm. The amount of delay composition (0.64 g) and loading pressure (184.6 MPa) remained constant so that the resulting columns, including the black powder input and output layers, were all 10.2 mm long. The inverse burning rate of this composition in the HHS housing is 7.70 s cm⁻¹, which corresponds to a burning rate of 0.13 cm s⁻¹. The burning rates in the aluminum and stainless steel tubes were only 6% and 2% greater, respec-

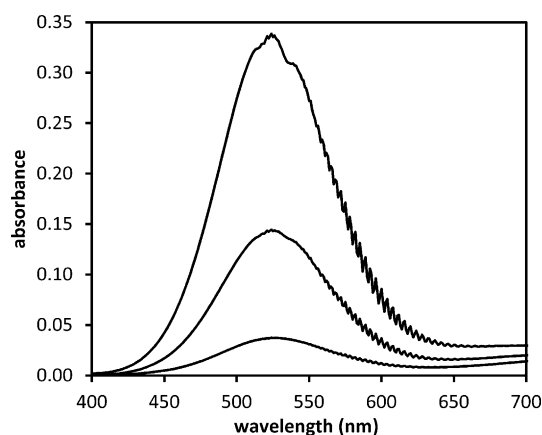


Figure 6. Visible spectra of I₂ vapor above ejected residue after burning a 40% W, 25% Sb₂O₃, 35% KIO₄, + 3% calcium stearate composition. Room temperature (bottom line) and two higher temperatures (middle and top lines).

tively. The gassy nature of the composition likely contributes to this insensitivity to housing material and configuration. Vented gases remove heat from the system that would otherwise be transferred in part to the housing walls [24].

3.4 Formation of I₂

These delay compositions emit purple-tinged smoke as they burn, leaving a hole down the center of the burnt column with residue remaining along the walls of the housing. A 40% W, 25% Sb₂O₃, 35% KIO₄, + 3% calcium stearate composition was loaded in aluminum tubes without black powder layers and ignited directly with an electrically heated wire. Purple I₂ crystals were deposited on the walls of a stainless steel cup when ejected residue was captured. These crystals sublimed rapidly from the warm residue when it was left in open air.

The characteristic visible spectrum of I₂ vapor [25] was observed when fresh residue was placed inside a gas cell (Figure 6). Even at room temperature, the purple vapor was visible above the residue and its color intensified as the cell was heated. I₂ formation is a general feature of the W/KIO₄ pyrotechnic reaction and is not contingent on the presence of Sb₂O₃. Binary W/KIO₄ mixtures, as unconsolidated powders, ignite with a bright flash and produce copious amounts of purple I₂ vapor and smoke. While it is a solid at room temperature, I₂ is significantly volatile and is released as a gas upon formation, thus contributing to the gassy nature of these delay compositions.

4 Conclusions

The W/Sb₂O₃/KIO₄/lubricant system displays a wide range of burning rates depending on tungsten content, oxidizer

ratio, lubricant identity, and lubricant level. Production of I_2 from the W/KIO_4 reaction makes the system gassy, regardless of which lubricant is used. Of all the lubricants tested, calcium stearate retarded burning rates the most, and this lubricant was used to demonstrate inverse burning rates out to 15 s cm^{-1} . Importantly these slow rates were achieved in the hand-held signal delay housing, which is a massive heat sink that readily quenches other slow-burning delay compositions. The development and application of highly tunable pyrotechnic delay systems such as this one is an ongoing area of research in our laboratories.

Symbols and Abbreviations

HHS	Hand-held signal
SEM	Scanning electron microscopy
SEI	Secondary electron imaging
VAAR	Vinyl alcohol/acetate resin
PTFE	Polytetrafluoroethylene
keV	Kiloelectronvolt
μm	Micrometer
MPa	Megapascal
kpsi	Kilopound per square inch
%-TMD	Density as percent of theoretical maximum

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